TRACE ELEMENT CONCENTRATIONS OF SOME PLANTS FROM THE MAUMEE BASIN, OHIO

Senior Thesis
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By
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ABSTRACT

Forty-six plant samples collected from the Maumee River Basin, Ohio, were analyzed with an atomic absorption spectrophotometer to determine the concentration of the following elements: copper, nickel, lead, cadmium, chromium, strontium, and calcium. The result is a body of data which serves as a general indication of the extent to which plants influence the trace element concentration in a hydrologic system. The method of preparing organic samples for spectrophotometric analysis has been refined and the procedure reported. Lists of the data with sample description are included, with tables of maximum, mean, and minimum concentration values. Additional charts and maps are included in attempts at correlation both within this data, and with that found in the literature. A computer program for execution of the Beer's Law conversion for calculating concentrations in milligrams per liter and micrograms per gram from strip chart peak heights is attached as an appendix.

INTRODUCTION

Forty-six plant samples collected from the major rivers of the Maumee Basin, Ohio, have been analyzed in an attempt to show to what extent plants affect the concentrations of trace elements in a hydrologic system. A Perkin-Elmer Model 303 atomic absorption spectrophotometer was used to analyze the samples for copper, lead, nickel, cadmium, chromium, strontium, and calcium.

Similar work has already been done on the trace element concentrations of water, sediment, and bedrock of the Maumee Basin, and this project is intended to add to this body of information by studying one of the many biologic factors which influence the hydrologic system. There may possibly be correlations between the data obtained in this study of plants and the recently accumulated information concerning water, sediment, and bedrock. However, due to the limited amount of data available at this time, only a few correlations will be attempted in this paper. The major objective of this study, therefore, was simply to determine to what extent,

that is, in what concentrations, do plants accumulate trace elements from water and sediment.

As the research progressed, a second objective was incorporated. An efficient method for preparing organic samples for spectrophotometric analysis was needed. Through interviews, research of the literature, and considerable experimentation, the technique of sample preparation was somewhat refined.

This paper will include: (1) a description of sample collection, including the types of plants used, the location, and the reason for their collection, (2) a discussion and evaluation of sample preparation techniques, (3) a presentation of the actual data, (4) some correlations with other data, (5) a summary and some conclusions, and (6) an appendix demonstrating the method used in converting strip-chart peak heights into concentrations in micrograms of trace element per gram of dried plant sample.

Acknowledgments

The writer wishes to express his appreciation to the many individuals whose help made this report possible. My sincere thanks to Dr. W. A. Pettyjohn for his direction and advice, and to Thomas Schultz and Gerald Shearer, graduate students, whose help in the Geohydrology Laboratory was invaluable. Also, to the many other members of the Department of Geology, especially Dr. G. Faure, Dr. J. Sutter, and E. Tremba, graduate student, for their help in the area of geochemistry,

goes much appreciation. The suggestions of Dr. J. Serif, Chairman of the Department of Biochemistry, were most helpful, as were all those from the many members of the Departments of Biology and Agronomy with whom information was exchanged in the course of this project.

Funds for transportation to the field area were supplied by the Friends of Orton Foundation.

SAMPLE COLLECTION

A total of fifty samples were collected from the Ottawa, Blanchard, Auglaize, Tiffin, and Maumee rivers. Forty-six of these samples were analyzed for trace elements. Samples 1-27 were collected on January 8, 1972, samples 28-34 on January 9, samples 35-44 on March 19, and samples 45-50 on April 23, 1972.

The first 44 samples were collected from the river waters, or when this was impossible, from the bank sediments. Most of the samples were collected near cities to detect any anomalies in concentrations downstream from upstream. Due primarily to bedrock river channels and the season, vegetation was scarce, and it was impossible to collect the same plant type at each location. It also proved to be beyond the scope of this investigation to identify each plant exactly. These deviations from a more ideal sample collection lend greatly to the generality of the data, and it should be reemphasized that its meaning is most useful as a general indicator of the role of plants in a trace

element investigation.

Samples 45-50 were collected and analyzed in an attempt to establish "normal" concentrations for plants of the area in question. These samples were collected well out of the influence of river water, and, as often as possible, above elevation 720 feet (the highest accessible elevation in the area). It seems likely that these are good indicators of normal concentrations of trace elements in these plants, that is, the concentration in plants not affected by any mineral source other than groundwater and soil. The example grass plants analyzed best illustrates the worth of the background samples. Samples 47 and 50 were both grass samples collected as background from different parts of the basin. When compared to the other grass samples, it becomes obvious that, in most cases, when the concentrations are high, they are still in the same general order as the background samples. When the values are low, they nearly always fall within the high and low background values. A more striking similarity for all the samples is the value for cadmium. Out of fourteen overall samples, eight showed only trace amounts (as did the background samples). The value for cadmium was never higher than 6 ug/g for any grass sample.

To make this comparison clearer, the following table compares the background samples with one sample showing high concentrations, and one showing low concentrations.

Element	Samples and Concentrations			
	Bac-47	Bac-50	M-27	M-29
Cu	17.125	8.888	13.720	44.746
Ni	3.627	12.852	7.892	50.317
Pb	13.620	9.694	6.124	11.015
Cd	Trace	Trace	Trace	1.725
Cr	2.354	1.613	3.873	9.023
Sr	199.750	5.100	---	21.941
Ca	203.657	244.484	---	132.283

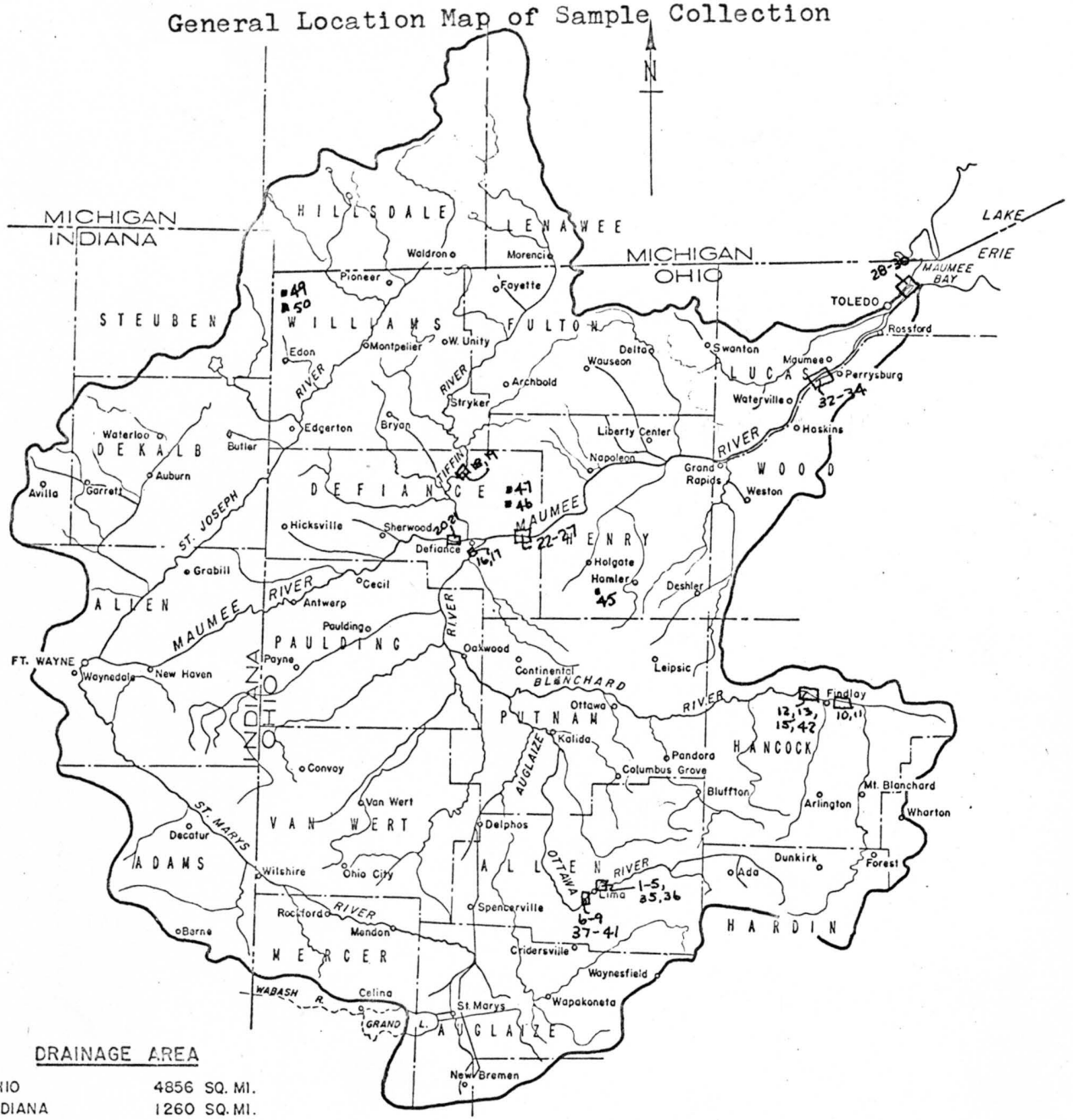
Certainly, there is no strict proportional relationship here, probably due to the many variables involved. There are some definite trends, however. For example, it may be said that since the two background samples were not affected by river water, and are very similar in their concentrations, they seem to be "normal" or average concentrations. Since M-27 very nearly agrees with the background samples, it may be considered to have about normal concentrations. On the other hand, M-29 is higher in most cases than the background samples, but has near the normal concentration of lead. It is in this manner that the background samples will be used subsequently.

It may be advantageous to the reader to explain the notation used in sample labeling at this time. The plants were assigned a number, which is merely the order of collection, preceeded by a letter, corresponding to the first letter of the name of the river from which the sample was collected.

For example, B-15 indicates that the fifteenth sample was collected from the Blanchard river. A-16 means that the next sample was taken from the Auglaize river, and so on. Bac-45 indicates that the forty-fifth sample was a background sample.

Map I

General Location Map of Sample Collection

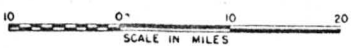


DRAINAGE AREA

OHIO	4856 SQ. MI.
INDIANA	1260 SQ. MI.
MICHIGAN	470 SQ. MI.
TOTAL IN BASIN	6586 SQ. MI.

MAUMEE RIVER DRAINAGE BASIN

LOCATION PLAN
MAUMEE RIVER DRAINAGE BASIN



SAMPLE PREPARATION

The second objective of this research project was to refine the technique of preparing organic samples for analysis with an atomic absorption spectrophotometer. This involves the complete solution of all tissues to be analyzed. To be efficient, a preparation method should be, first of all, quantitative. Beyond this, it should be easily accessible, which usually implies inexpensive, and fast enough to allow a number of samples to be prepared and analyzed in a reasonable amount of time. It was with these criteria in mind that a method was sought after.

There are two suggested methods for sample preparation in the atomic absorption manual supplied by Perkin-Elmer. The first of these is the perchloric acid method, in which organic matter is simply digested in reagent-grade perchloric acid. The second method suggested in the spectrophotometry manual involved a dry ashing procedure in a hot

muffle furnace, and then wet digestion in hydrochloric and nitric acids.

The perchloric acid method seems to be the easiest, fastest, and probably the most quantitatively accurate of any method, because there are less possibilities for contamination during preparation, and low temperatures are used. The major fault of the perchloric acid method is that the use of such a strong organic oxidizing agent is quite dangerous. As a result, a special hood is required. Sice such special equipment was not available for use in this project, an alternate method had to be found. Lack of a muffle furnace prevented the use of the second method suggested by Perkin-Elmer.

A variation of the muffle furnace method was being used by Gerald Shearer, a graduate student in the Department of Geology at Ohio State, and was the first method used in this project. The procedure involved the use of Erlenmeyer flasks and Fisher burners instead of the muffle furnace. After the flasks were weighed, the oven-dried plant sample was added. The total weight minus the weight of the flask yeilded the dry weight of the sample. The flasks were then heated over burners until only a white powdery residue and black tars and oils remained. When the flasks had cooled, 25 ml. of a 1:1 solution of hydrochloric and nitric acids were added. This mixture was then boiled and concentrated by evaporation until all residues were dissolved. The

remaining solution was washed from the flasks with demineralized filtered water to a volume of 25 ml.

The time involved in the preceeding method from weighing the flasks until the sample was ready for analysis was from ten to twelve hours. Since relatively high temperatures were used, there was the constant danger of flasks breaking, and several samples were lost in this way. With constant attention over the ashing and solution period, a maximum of eight samples could be prepared. Other inadequacies of the method include the ever-present possibility of contamination, and the probable loss of all volitile trace elements such as mercury and cadmium, which have relatively low vaporization temperatures. These problems leave the quantitativeness of the modified muffle furnace method somewhat in doubt.

The second method which was used in this project resulted from conferences with members of the departments of Agronomy and Biochemistry of The Ohio State University. Dr. Serif, Chairman of the Department of Biochemistry, suggested the use of boiling sulfuric acid as a solvent, and hydrogen peroxide as an oxidizing agent. In several trials, it was found that the reaction of hydrogen peroxide and sulfuric acid was so violent that samples were easily lost by boiling over. At this point, concentrated nitric acid was substituted for hydrogen peroxide as the oxidizing agent.

The sulfuric-nitric digestion method included the same weighing procedure as the dry ashing method described earlier, followed by the addition of 25 ml. of concentrated

sulfuric acid. The best results were achieved when the samples were left covered to stand overnight, allowing the plant material to become saturated with the acid, and be partially disolved, but this was not necessary. The flasks were then heated over low flame, and the sample digested as the sulfuric acid became concentrated. Nitric acid was then added by drops until all undisolved particles were in solution. The flasks were then washed to 25 ml. Using this process, eight samples could be prepared in one hour.

Quantitative problems arose from the use of the sulfuric-nitric acid method which had not been indicated by those who had claimed to be using this method in preparation for spectrophotometric analyses. The problem was discovered while preparing standard and blank solutions. The samples prepared with sulfuric and nitric acids were considerably more viscous than those prepared by the dry ashing method. Therefore, less sample was aspirated in a given time. To yield realistic results, the standards were made of a comparable viscosity. The real problem arose when it was discovered that undiluted sulfuric acid would yield a peak height of about five units on the strip-chart at a scale expansion of ten. This occurred at all wavelengths of light used in analysis. As demineralized filtered water was added to dilute the sulfuric acid, a less viscous liquid resulted, more was aspirated per unit of time, and the peak height became higher. The strip-chart peak heights grew proportionally

higher for each dilution of the acid, until the viscosity became incomparable withthat of the actual samples, and further testing became meaningless.

Since there was no way of determining the source of contamination of the acid (new bottles were tried, and peak heights resulted under all wavelengths as before), nor precisely how much error due to the acid had been introduced into each sample, an estimation on the basis of viscosity was made. The sulfuric acid in the samples was more concentrated than originally, due to evaporation during boiling, and therefore a ratio of two parts sulfuric to one part demineralized filtered water was used for the blank solution and standard preparation. Some samples were prepared with sulfuric acid and hydrogen peroxide in hopes of eliminating this problem, but the same difficulties arose.

The disadvantages of the sulfuric-nitric or sulfuric-hydrogen peroxide digestion method finally proved too numerous to be useful. Although the method was fast and inexpensive, its quantitative results are questionable, and the seventeen samples which were prepared in this manner (23, 25, and 28-42) should probably not be taken as absolute values. Most of the error was probably eliminated by the addition of an approximately equivalent factor in the standards, but as was stated before, the factor was only an estimate. A possible way of eliminating the quantitative error in this type of preparation would be to use specially

distilled sulfuric acid which is guaranteed pure. This, however, greatly increases the expense, especially when a fairly large number of samples are involved.

Toward the end of the project, a third method of sample preparation was attempted. This method again used the same weighing procedure as the other methods, but the dried plants were this time digested by boiling in 25-50 ml. of concentrated nitric acid, and oxidized by the addition of 30% hydrogen peroxide. This proved to be the most acceptable technique of all. The time involved is even less than the sulfuric-nitric acid digestion, and less heat is needed as well. This reduces the possibility of volatile loss. The nitric-hydrogen peroxide method is inexpensive, and requires only a conventional type hood to remove noxious gases. From all indications, the nitric acid-hydrogen peroxide method is quantitatively sound.

One other method might be mentioned here for completeness. Woodrow Krueger, graduate student of Ohio State's Department of Biology, made use of a low temperature muffle furnace for preparation of organic samples for mercury concentration analyses. This process requires unattended overnight ashing in the furnace, and solution in any suitable acid. The apparatus required for this method was prohibitively expensive,

If all of these processes were rated in order of descending efficiency, as it has been defined in this paper, the nitric acid-hydrogen peroxide method would head the list.

The dry ashing-acid solution method described first would follow, and the muffle furnace-acid solution method would be third. The perchloric acid method would be next, followed by the low temperature muffle furnace method. The sulfuric-nitric and sulfuric-hydrogen peroxide methods would not be recommended without further refinement, and use of distilled reagent. It must, of course, be remembered that the perchloric acid method is probably equal, if not superior, to the nitric acid-hydrogen peroxide method, if the proper equipment (hood) is accessible.

DATA

Introduction

The data collected from spectrophotometric analyses of 46 plant samples are presented in the following section of this paper. Preceding the list of concentrations for each sample is a brief description of the sample, including the date and place of collection, general name of the plant type, and digestion method (as described in the previous section) used in preparing the sample. It should be noted that all concentrations are in micrograms per gram (ug/g) of trace element in the dried plant sample.

The following form of data presenteation was designed to help the reader by having all information pertinent to each sample in one place. This should prove helpful in comparing samples, or correlating the analytical data with location maps. The quadrangle from which the sample was collected has been included to aid any future attempts to elaborate on this work. The exact collection locations are marked on the

quadrangle maps on file in the Geohydrology Laboratory, Room 16, Mendenhall Lab, The Ohio State University. A more general location map is included in this section.

The notation "Dry ash" at the end of the sample description indicates that the sample was prepared for analysis by the first method which was described at length in the previous section. Similarly, "Sulfuric-nitric" or Sulfuric-hydrogen peroxide" indicates that one of the two sulfuric acid digestion methods was used, and "Nitric" means that the sample was prepared by the nitric acid-hydrogen peroxide method.

Three dashes (---) after the element symbol indicates that the sample was not analyzed for that particular element. This was usually due to the lack of enough sample to permit complete analysis. Calcium and strontium were not among the elements originally intended for analysis in this project, and data is only available for samples 23, 25, and 28-50. The decision to analyze for these additional elements is explained later in this section.

The computer program which is included as an appendix applies the Beer's Law conversion for calculating trace element concentrations in milligrams per liter of solution, and micrograms per gram of dried plant sample from peak heights recorded on the spectrophotometer strip chart. Very briefly, this entails a comparison of peak heights received from the aspiration of sample solutions with peak heights from aspiration of standard solutions of known concentration.

The comparison is made in the form of a best fit curve. Occasionally, the y intercept, B, of the graph is greater than zero, and also greater than the absorbance value, AXQI of a sample. When this occurs, AXQI for the sample lies off of the curve, below zero and the y intercept, and a negative concentration value results. In fact, however, there is a concentration greater than zero present. The program has therefore been set up to print "TRACE" in such situations. (See line 35 of the computer program appendix.)

Sample O-1

Collected January 8, 1972 from the Ottawa River, east of Lima (Cairo Quadrangle), Ohio.
ROOTS of an aquatic plant found growing on channel bottom. Dry ash.

Cu	9.024
Ni	0.977
Pb	1.820
Cd	Trace
Cr	---
Sr	---
Ca	---

Sample O-2

Collected January 8, 1972 from the Ottawa River, east of Lima (Cairo Quadrangle), Ohio.
SYCAMORE BUDS (new branch growth), growing on anisland. Dry ash.

Cu	15.721
Ni	0.828
Pb	7.096
Cd	Trace
Cr	0.206
Sr	---
Ca	---

Sample O-3

Collected January 8, 1972 from the Ottawa River, east of Lima (Cairo Quadrangle), Ohio.
ROOTS and STEMS of a grassy plant found growing in an eddy pool. Dry ash.

Cu	12.036
Ni	2.231
Pb	3.499
Cd	0.127
Cr	1.155
Sr	---
Ca	---

Sample O-4

Collected January 8, 1972 from the bank of Lost Creek at its junction with the Ottawa River, east of Lima (Cairo Quadrangle), Ohio.
TREE BRANCHES. Dry ash.

Cu	10.529
Ni	0.841
Pb	4.189
Cd	Trace
Cr	0.253
Sr	---
Ca	---

Sample O-5

Collected January 8, 1972 from the bank of Lost Creek at its junction with the Ottawa Raiver, east of Lima (Cairo Quadrangle), Ohio.
GRASS. Dry ash.

Cu	15.538
Ni	5.048
Pb	16.447
Cd	Trace
Cr	3.509
Sr	---
Ca	---

Sample O-6

Collected January 8, 1972 from the Ottawa River, west of Lima (Cridersville Quadrangle), Ohio.
TREE BRANCHES from tree growing on the bank. Dry ash.

Cu	12.460
Ni	1.577
Pb	6.823
Cd	0.056
Cr	0.604
Sr	---
Ca	---

Sample O-7

Collected January 8, 1972 from the Ottawa River, west of Lima (Cridersville Quadrangle), Ohio.
TREE BRANCHES (new growth), from a small tree growing on a normally submerged island. Dry ash.

Cu	11.487
Ni	2.963
Pb	---
Cd	---
Cr	1.266
Sr	---
Ca	---

Sample O-8

Collected January 8, 1972 from the Ottawa River, west of Lima (Cridersville Quadrangle), Ohio.
GRASS, rooted at midstream, across from sewage disposal plant. Dry ash.

Cu	45.786
Ni	82.689
Pb	53.080
Cd	6.000
Cr	62.534
Sr	---
Ca	---

Sample O-9

Collected January 8, 1972 from the Ottawa River, west of Lima (Cridersville Quadrangle), Ohio.
WEEDS rooted in stream across from sewage disposal plant. Dry ash.

Cu	37.967
Ni	112.679
Pb	113.121
Cd	7.256
Cr	81.961
Sr	---
Ca	---

Sample B-10

Collected January 8, 1972 from the Blanchard River, east of Findlay (Arcadia Quadrangle), Ohio.
GRASS found growing in an eddy pool. Dry ash.

Cu	3.244
Ni	1.265
Pb	15.128
Cd	Trace
Cr	0.363
Sr	---
Ca	---

Sample B-11

Collected January 8, 1972 from the Blanchard River, east of Findlay (Arcadia Quadrangle), Ohio.
BRANCHES and BUDS from shrub growing along foot bridge. Dry ash.

Cu	18.340
Ni	1.262
Pb	9.858
Cd	0.859
Cr	0.294
Sr	---
Ca	---

Sample B-12

Collected January 8, 1972 from the Blanchard River, west of Findlay (Findlay Quadrangle), Ohio.
AQUATIC PLANT with no roots, found floating freely in mid-stream. Easily relocated by characteristic morphology. Dry ash.

Cu	136.166
Ni	390.082
Pb	79.856
Cd	14.358
Cr	63.522
Sr	---
Ca	---

Sample B-13

Collected January 8, 1972 from the Blanchard River, west of Fidlay (Findlay Quadrangle), Ohio.
DANDELIONS growing partially submerged on river bank.
Dry ash.

Cu	14.449
Ni	---
Pb	18.069
Cd	Trace
Cr	1.604
Sr	---
Ca	---

Sample B-15

Collected January 8, 1972 from the Blanchard River, west of Findlay (Findlay Quadrangle), Ohio.
DANDELIONS growing on river bank. Dry ash.

Cu	16.849
Ni	15.055
Pb	27.353
Cd	Trace
Cr	0.744
Sr	---
Ca	---

Sample A-16

Collected January 8, 1972 from the Auglaize River, southwest of Defiance (Junction Quadrangle), Ohio.
ROOTS, or starchy tubers, found growing in sandy inlet near boat launching ramp off Rt. 111. Dry ash.

Cu	41.784
Ni	8.207
Pb	53.751
Cd	Trace
Cr	7.631
Sr	---
Ca	---

Sample A-17

Collected January 8, 1972 from the Auglaize River, southwest of Defiance (Junction Quadrangle), Ohio.
GRASS rooted in sandy inlet near boat ramp off Rt. 111.
Dry ash.

Cu	78.929
Ni	83.040
Pb	25.058
Cd	Trace
Cr	14.707
Sr	---
Ca	---

Sample T-18

Collected January 8, 1972 from the Tiffin River, northwest of Defiance (Defiance West Quadrangle), Ohio.
WEEDS (roots,stems,and leaves), rooted in a submerged part of river bank. Dry ash.

Cu	52.587
Ni	16.535
Pb	21.914
Cd	Trace
Cr	13.550
Sr	---
Ca	---

Sample T-19

Collected January 8, 1972 from the Tiffin River, northwest of Defiance (Defiance West Quadrangle), Ohio.
GRASS growing on river bank. This plant was the dominant flora both in and out of the water. Dry ash.

Cu	30.540
Ni	13.450
Pb	8.606
Cd	Trace
Cr	2.719
Sr	---
Ca	---

Sample M-20

Collected January 8, 1972 from the Maumee River, west of Defiance (Defiance West Quadrangle), Ohio. BRANCHES and BUDS from shrub rooted in channel bottom. Dry ash.

Cu	21.243
Ni	3.023
Pb	3.345
Cd	1.885
Cr	0.781
Sr	---
Ca	---

Sample M-21

Collected January 8, 1972 from the Maumee River, west of Defiance (Defiance West Quadrangle), Ohio. VIOLETS found growing on bank, ten feet from water on normally submerged part of floodplain. Dry ash

Cu	53.614
Ni	23.836
Pb	14.067
Cd	0.123
Cr	5.334
Sr	---
Ca	---

Sample M-22

Collected January 8, 1972 from the Maumee River, east of Defiance (Defiance East Quadrangle), Ohio. WEED (stems and roots), found growing on bank. Dry ash.

Cu	11.690
Ni	6.132
Pb	4.283
Cd	1.000
Cr	1.137
Sr	---
Ca	---

Sample M-23

Collected January 8, 1972 from the Maumee River, east of Defiance (Defiance East Quadrangle), Ohio. WEED (buds and stems), rooted in channel bottom. Sulfuric-nitric.

Cu	36.811
Ni	10.523
Pb	135.427
Cd	21.207
Cr	1.169
Sr	17.167
Ca	248.888

Sample M-24

Collected January 8, 1972 from the Maumee River, east of Defiance (Defiance East Quadrangle), Ohio. GRASS growing on normally submerged bank of State Park boat launching canal. Dry ash.

Cu	29.281
Ni	18.236
Pb	22.040
Cd	2.462
Cr	16.033
Sr	---
Ca	---

Sample M-25

Collected January 8, 1972 from the Maumee River, east of Defiance (Defiance East Quadrangle), Ohio. WEED growing on usually submerged bank of State Park boat launching canal. Sulfuric-nitric.

Cu	1.737
Ni	12.332
Pb	1.973
Cd	0.633
Cr	4.200
Sr	8.306
Ca	13.245

Sample M-26

Collected January 8, 1972 from the Maumee River, east of Defiance (Defiance East Quadrangle), Ohio. WEED (starchy roots, stems, and leaves), growing on bank of main channel. Dry ash.

Cu	27.691
Ni	6.809
Pb	5.474
Cd	Trace
Cr	1.518
Sr	---
Ca	---

Sample M-27

Collected January 8, 1972 from the Maumee River, east of Defiance (Defiance East Quadrangle), Ohio. GRASS growing on bank of main channel. Dry ash.

Cu	13.720
Ni	7.892
Pb	6.124
Cd	Trace
Cr	3.873
Sr	---
Ca	---

Sample M-28

Collected January 9, 1972 from the Maumee River, east of Toledo (Oregon Quadrangle), Ohio. CATTAIL ROOTS exposed along main channel. Sulfuric-nitric.

Cu	22.643
Ni	27.561
Pb	0.758
Cd	2.092
Cr	47.790
Sr	2.056
Ca	4.417

Sample M-29

Collected January 9, 1972 from the Maumee River, east of Toledo (Oregon Quadrangle), Ohio. GRASS found growing on bank of the Maumee at its junction with Lake Erie. Sulfuric-nitric.

Cu	44.746
Ni	50.317
Pb	11.015
Cd	1.725
Cr	9.023
Sr	21.941
Ca	132.283

Sample M-30

Collected January 9, 1972 from the Maumee River, east of Toledo (Oregon Quadrangle), Ohio. TREE BRANCHES from tree growing on bank of the Maumee at its junction with Lake Erie. Sulfuric-nitric.

Cu	Trace
Ni	0.000
Pb	Trace
Cd	0.000
Cr	65.477
Sr	119.609
Ca	333.138

Sample M-32

Collected January 9, 1972 from the Maumee River, southwest of Toledo (Maumee Quadrangle), Ohio. TREE BRANCHES from a tree rooted in channel sediment. Sulfuric-nitric.

Cu	45.897
Ni	6.247
Pb	20.184
Cd	12.519
Cr	2.149
Sr	11.298
Ca	66.403

Sample M-33$_A$ + B*

Collected January 9, 1972 from the Maumee River, southwest of Toledo (Maumee Quadrangle), Ohio. GRASS from main channel bank. Sulfuric-nitric.

	A		B
Cu	17.229	Cu	Trace
Ni	7.453	Ni	42.098
Pb	25,006	Pb	Trace
Cd	3.277	Cd	Trace
Cr	24.914	Cr	Trace
Sr	0.561	Sr	47.250
Ca	5.479	Ca	1481.601

Sample M-34

Collected January 9,1972 from the Maumee River, southwest of Toledo (Maumee Quadrangle), Ohio. WEEDS (roots and leaves), growing on main channel bank. Sulfuric-nitric.

Cu	0.000
Ni	0.000
Pb	231.836
Cd	Trace
Cr	Trace
Sr	117.512
Ca	3798.905

* In order to make a comparison of ug/g concentrations obtained from different weights of the same sample, different weight amounts (see appendix) of sample 33 were digested and analyzed during the course of the project. Obvious ug/g discrepancies occured, perhaps due to questionable analytical proceedure, or the fact different parts of the plant may have been concentrated in one sample or the other. It is my opinion that these values serve as a general indication of the trace element concentrations, but there is some question as to their quantitativeness.

E - Sample 0-35

Collected March 19, 1972 from the Ottawa River, east of Lima (Lima Quadrangle), Ohio.
WEEDS (roots), mostly submerged part of the bank, just east of pumping station. Sulfuric-nitric.

Cu	76.788
Ni	6.008
Pb	Trace
Cd	0.078
Cr	1.350
Sr	0.777
Ca	4.028

E Sample 0-36

Collected March 19, 1972 from the Ottawa River, east of Lima (Lima Quadrangle), Ohio.
WEEDS (roots, stems, and leaves), growing submerged, just east of pumping station. Sulfuric-nitric.

Cu	0.293
Ni	0.000
Pb	0.000
Cd	0.000
Cr	Trace
Sr	51.550
Ca	193.439

- Sample 0-37

Collected March 19, 1972 from the Ottawa River, west of Lima (Cridersville Quadrangle), Ohio.
TREE ROOTS taken from channel bottom, downstream from refinerydump, across from sewage disposal plant. Sulfuric-nitric.

Cu	578.379
Ni	83.602
Pb	62.981
Cd	125.494
Cr	266.937
Sr	10.282
Ca	16.685

Sample 0-38

Collected March 19, 1972 from the Ottawa River, west of Lima (Cridersville Quadrangle), Ohio.
WEED (stems and leaves), found growing in midstream downstream from refinery dump, across from sewage disposal plant. Sulfuric-hydrogen peroxide.

Cu	Trace
Ni	0.000
Pb	0.000
Cd	0.000
Cr	50.414
Sr	893.484
Ca	10,871.010

W - Sample 0-39

Collected March 19,1972 from the Ottawa River, west of Lima (Cridersville Quadrangle), Ohio.
GRASS growing in midstream, across from sewage disposal plant. Sulfuric-hydrogen peroxide.

Cu	863.912
Ni	41.455
Pb	Trace
Cd	2.356
Cr	417.883
Sr	0.761
Ca	5.472

W - Sample 0-40

Collected March 19, 1972 from the Ottawa River, west of Lima (Cridersville Quadrangle), Ohio .
GRASS growing midstream in front of refinery dump.
Sulfuric-hydrogen peroxide.

Cu	72.211
Ni	148.531
Pb	24.123
Cd	6.568
Cr	161.248
Sr	1.276
Ca	6.806

Sample O-41

Collected March 19,1972 from the Ottawa River, west of Lima (Cridersville Quadrangle), Ohio.
BRANCHES taken from shrub growing midstream across from sewage disposal plant. Sulfuric-hydrogen peroxide.

Cu	Trace
Ni	1.979
Pb	0.000
Cd	0.165
Cr	Trace
Sr	53.489
Ca	74.101

Sample B-42

Collected March 19,1972 from the Balnchard River, west of Findlay (Findlay Quadrangle), Ohio.
AQUATIC PLANT with no roots, found floating freely. Identical plant and location as Sample B-12. Sulfuric-hydrogen peroxide.

Cu	Trace
Ni	0.000
Pb	Trace
Cd	0.000
Cr	Trace
Sr	429.300
Ca	1211.871

Sample Bac-45

Collected April 23, 1972 from a drainage ditch off Co. Rd. 11, 100 feet south of Rt. 18, Hamler Quadrangle, Ohio.
CATTAIL ROOTS. Nitric.

Cu	7.035
Ni	1.020
Pb	2.055
Cd	Trace
Cr	0.850
Sr	8.279
Ca	140.715

Sample Bac-46

Collected April 23, 1972 from a field off of Thieroff Rd., between Co. Rds. 18 and 19, Florida Quadrangle, Ohio.
DANDELIONS (roots,stems, and leaves). Nitric.

Cu	14.185
Ni	1.305
Pb	4.757
Cd	Trace
Cr	0.995
Sr	8.916
Ca	135.715

Sample Bac-47

Collected April 23, 1972 from field off Thieroff Rd., between Co. Rds. 18 and 19, Florida Quadrangle, Ohio.
GRASS. Nitric.

Cu	17.125
Ni	3.627
Pb	13.620
Cd	Trace
Cr	2.354
Sr	199.750
Ca	203.657

Sample Bac-49

Collected April 23, 1972 from wooded area near cemetery on Mulligan's Bluff Rd., Evansport Quadrangle, Ohio.
White dogtooth lily (Erithronium Albidum), roots (bulbs), stems, and leaves. Nitric.

Cu	5.275
Ni	0.309
Pb	0.452
Cd	Trace
Cr	0.211
Sr	4.354
Ca	366.266

Sample Bac-50

Collected April 23, 1972 from wooded area near cemetery on Mulligan's Bluff Rd,, Evansport Quadrangle, Ohio. GRASS. Nitric.

Cu	8.888
Ni	12.852
Pb	9.694
Cd	Trace
Cr	1.613
Sr	5.100
Ca	244.484

TABLE I

Table of Maximum, Mean, and Minimum Values for Each Element

Element		Concentration (ug/g)	Sample Number
Cu	Max.	863.912	0-39, grass
	Mean	55.082	
	Min.	0.000	M-34, weeds
Ni	Max.	390.082	B-12, aquatic plant
	Mean	27.307	
	Min.	0.000	M-30, M-34, M-36 0-38, B-42
Pb	Max.	231.836	M-34, weeds
	Mean	23.881	
	Min.	0.000	0-36, 0-38. 0-41
Cd	Max.	125.494	0-37, tree roots
	Mean	4.672	
	Min.	0.000	M-36, 0-36, 0-38, B-42
Cr	Max.	417.883	0-39, grass
	Mean	29.864	
	Min.	Trace	$M\text{-}33_b$, M-34, 0-36 0-41, B-42
Sr	Max.	893.484	0-38, weed
	Mean	91.501	
	Min.	0.561	$M\text{-}33_a$, grass
Ca	Max.	10,871.010	0-38, weed
	Mean	889.020	
	Min.	4.028	0-35, weed

Calcium - Strontium Analysis

During the analysis of the second set of samples (23, 25, and 28- 44) for the usual five elements, copper, nickel, lead, cadmium, and chromium, an interesting phenomenon was noticed. Very low concentrations of the five usual elements appeared in several samples, and they seemed always to be accompanied by a bright red-orange flame during aspiration. The flame color led me to suspect the presence of strontium in the samples, and the decision was made to analyze the remaining samples for this element.

There was some question as to the origin of the strontium concentrations, and it was reasoned that the bedrock of the Maumee Basin was an excellent possibility. Since strontium and calcium are very similar in atomic and ionic sizes, and also in electronegativity, they may often enter the same kind of atomic sites in a compound. Since the bedrock of the Maumee Basin is largely Silurian and Devonian limestone and dolomite, there is a good chance that this was the source. Analysis of the bedrock for strontium could yield conclusive results.

It was thought that the concentrations of calcium might prove valuable, and analyses for this element were done subsequently. Calcium was found to be present in relatively high concentrations. This was attributed to the use of calcium for many different functions in plants (for example, plants form a compound, calcium pectate, which forms rigid covers for root hairs, and also cements cell

walls).

In the majority of cases, calcium and strontium were present in very high concentrations while the other elements showed relatively low concentrations. Several considerations were taken into account at this point. Replacement of other ions by calcium and strontium was considered at first, but this was reasoned unlikely due to the widely differing atomic and ionic properties involved. The second consideration was an analytical one. Since the heats of vaporization of calcium and strontium are relatively low (36.74 and 33.8 k-cal/g-atom, respectively, as compared to 91.0k-cal/g-atom for nickel, for example), it is likely that these were driven off in preparation by the dry ash method. This no doubt accounts for the fact that no noticably strong red-orange flames were detected during the analysis of the first set of samples. Since less heat was used in the preparation of the second set of samples, it is probable that less, if any of the calcium and strontium was lost.

High concentrations of calcium and strontium producing bright-red-orange flames becomes important, because there is the possibility that the secondary or even less intense spectral lines of calcium and strontium may have interfered with the analytical wavelengths of the less abundant elements. This would mask the true concentrations of the less abunbant elements. Table II shows the primary (that used for analysis) and secondary wavelengths of calcium and strontium compared

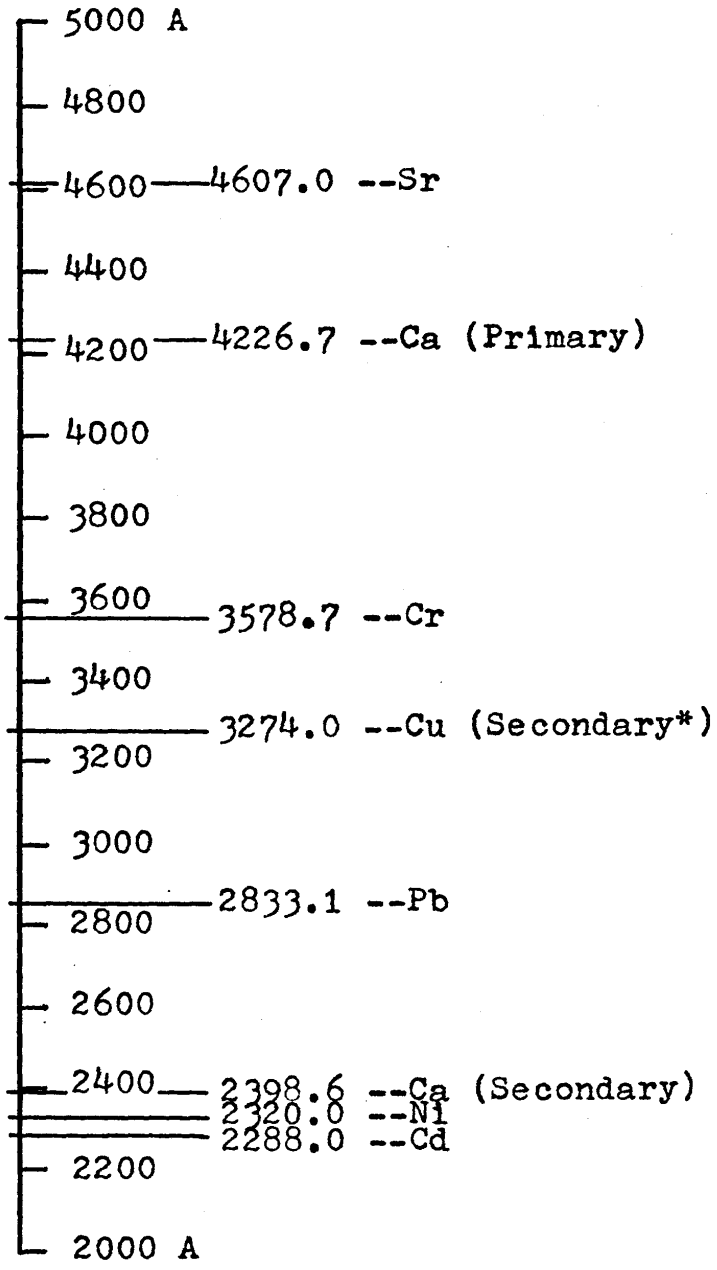
with the primary wavelengths of the other five elements. Time did not permit further investigation of this problem in the laboratory, but some statistical methods were applied in an attempt to detect a pattern in the varying concentrations.

If it is true that the analytical wavelengths overlap with other spectral lines, it seems reasonable that the amount of masking should somehow be proportional to the concentrations, or the intensity of the interfering secondary lines. It was expected, therefore, that as the amount of calcium and strontium in the samples increased, the apparent concentrations of the other trace elements would decrease in some relative, perhaps linear, way.

Table III gives the ratios of the summation of the concentrations (ug/g) of copper, nickel, lead, cadmium, and chromium to the sum of the calcium and strontium concentrations. Attempts were made to graph the results, but the number of data points proved too few to allow a reasonable estimate of the relationship. The information in Table III is included as possible information for further work. Other methods of statistical inspection of the data were applied, but the results were not note worthy.

TABLE II

Spectra Wavelength Comparison Chart



*Primary wavelengths are used for analysis in every case except that of Cu, for which the Secondary wavelength is used due to use of multi-element lamp.

TABLE III

Ratios of Summations of Concentrations

Sample	ΣI Cu+Ni+Pb+Cd+Cr	ΣII Sr+Ca	$\frac{\Sigma I}{\Sigma II}$
M-23	205.157	266.055	0.771
M-25	20.875	21.551	0.968
M-28	100.844	6.473	15.579
M-29	116.826	154.224	0.757
M-30	65.477	452.747	0.144
M-32	86.996	77.701	1.119
$M-33_a$	77.879	6.040	12.893
$M-33_b$	42.098	1528.851	0.027
M-34	231.836	3916.417	0.059
O-35	84.224	4.805	17.528
O-36	0.293	244.989	0.001
O-37	1117.393	26.967	41.435
O-38	50.414	11764.494	0.004
O-39	1325.606	6.233	212.675
O-40	412.681	8.082	51.061
O-41	2.144	127.590	0.016
B-42	0.000	1641.171	0.000
Bac-45	10.960	148.994	0.073
Bac-46	21.242	144.631	0.146
Bac-47	36.726	403.407	0.091
Bac-49	6.247	370.620	0.016
Bac-50	33.047	249.584	0.139

CORRELATION OF THE DATA

Application Within This Project

As was mentioned earlier, the majority of samples analyzed in the course of this project serve primarily as general indicators of the types of concentrations whcih may be expected in plants, and to what degree plants might influence a trace element study of a hydrologic system. It might be desirable to do a study using one specific plant to detect changes in concentrations upstream from down, above and below cities, or perhaps at different periods of flow. Many analyses would have to be made over a long period of time to obtain such data. However, a few patterns of this type may be detected from a correlation of the data accumulated from the analyses of grass samples collected for this project. Grass was the only plant collected often enough (13 times) to enable reasonably valid comparisons to be made of concentrations in the same plant type. A location map of the grass samples and Table IV, of their concentrations,

have been supplied to aid in correlation. In the following comparisons, the concentrations of samples Bac-47 and Bac-50 will be assumed to be normal concentrations.

It appears that those samples collected upstream of the larger cities in the area had lower concentrations (note samples 0-5, B-10, and T-19) than those collected immediately downstream (samples 0-8, 0-39, and 0-40). Exceptions do occur, such as in the case of sample A-17, collected upstream from Defiance, Ohio, and showing relatively high concentrations of almost all elements. Samples M-24, M-27, and M-29 are higher than normal, which might be expected from their locations downstream of cities, but they are relatively low in comparison to other downstream samples. Such discrepancies could be explained by dilution, since M-24, M-27, and M-29 were collected farther downstream from cities than were the other downstream samples, but speculation of this type will be attempted in a later section. Samples collected upstream from cities were near or below the normal concentrations for most elements. Samples collected downstream were higher than normal in almost every case.

The samples collected near Lima (0-5, 0-8, 0-39, and 0-40) are the most varied in concentration, and demonstrate the difference that location can make very well. It is interesting to note that the downstream samples were collected at two different times, possibly indicating that concentrations below lima are consistantly high. No grass samples were

collected downstream from Findlay, but the concentrations for samples B-13 and B-15 (dandelions, collected downstream from Findlay) showed slightly higher than normal (as in sample Bac-46) trace element concentrations for that plant type. This would tend to support the general pattern. The grass samples collected above and below Defiance were widely separated, coming from three different rivers, but show the same general trend in concentrations, rising downstream. Samples M-24 and M-27 may be considered upstream from Toledo, though they are far removed from the city, and are accordingly lower in concentrations than sample M-29, from the mouth of the Maumee River at Lake Erie.

Projects with this type of correlation in mind have been performed in attempts to locate ore bodies by concentration anomalies in plants in northwestern Canada (Warren, 1972). It is conceivable that the same method might be used to detect dangerous levels of pollution in urban areas. Of course, many more controls and a greater understanding of the plant biochemistry involved would be needed to make such a project meaningful.

TABLE IV

Trace Element Concentrations in Grass Samples

Normal Values

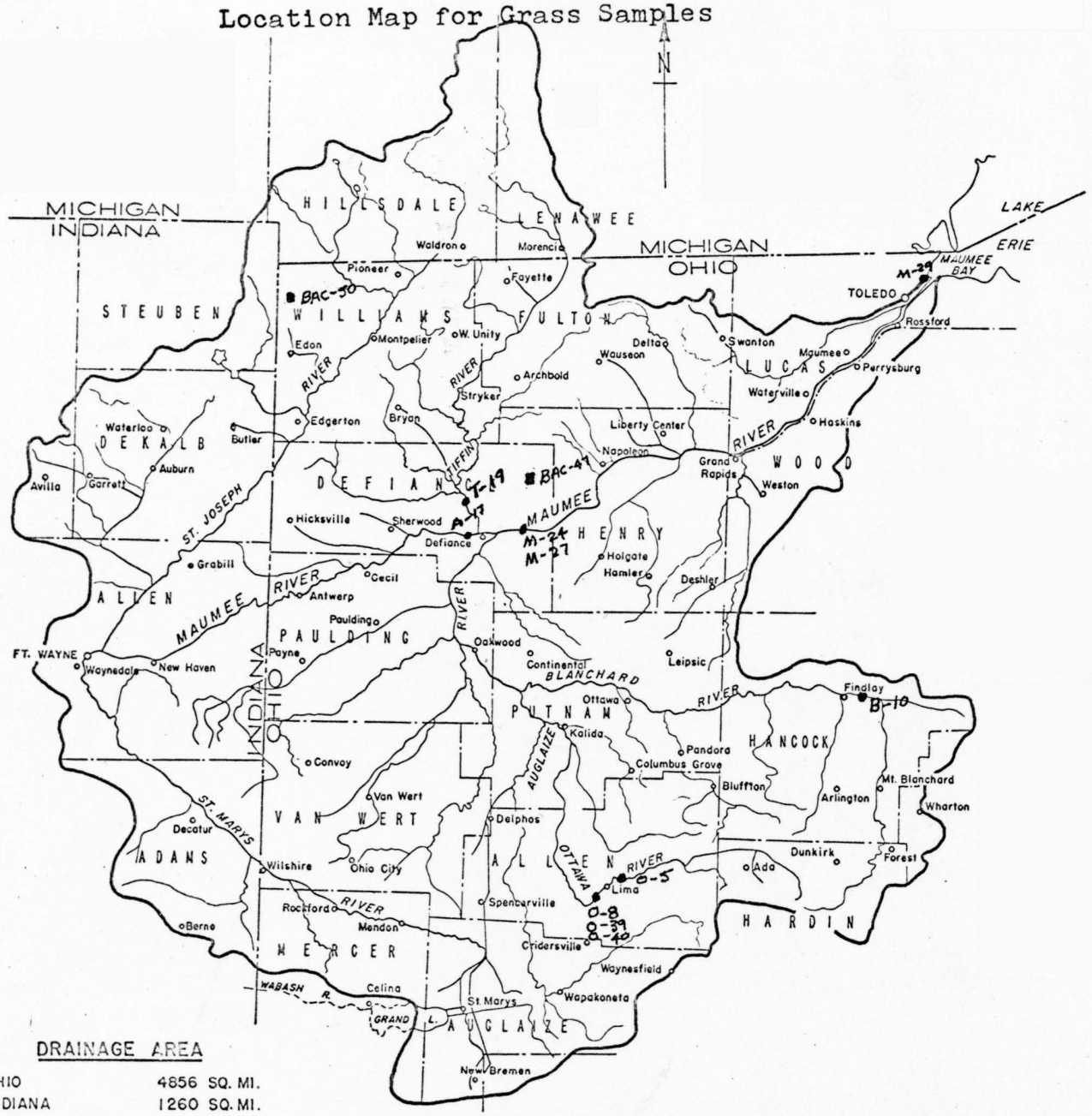
	Bac-47	Bac-50
Cu	17.125	8.888
Ni	3.627	12.852
Pb	13.620	9.694
Cd	Trace	Trace
Cr	2.354	1.613
Sr	199.750	5.100
Ca	203.657	244.484

	0-5	0-8	B-10	A-17	T-19
Cu	15.538	45.786	3.244	78.929	30.540
Ni	5.048	82.689	1.265	83.040	13.450
Pb	16.447	53.080	15.128	25.058	8.606
Cd	Trace	6.000	Trace	Trace	Trace
Cr	3.509	62.534	0.363	14.707	2.719
Sr	---	---	---	---	---
Ca	---	---	---	---	---

	M-24	M-27	M-29	0-39	0-40
Cu	29.281	13.720	44.746	863.912	72.211
Ni	18.236	7.892	50.317	41.455	148.531
Pb	22.040	6.124	11.015	Trace	24.123
Cd	2.462	Trace	1.725	2.356	6.568
Cr	16.033	3.873	9.023	417.883	161.248
Sr	---	---	21.941	0.761	1.276
Ca	---	---	132.283	5.472	6.806

Map II

Location Map for Grass Samples



DRAINAGE AREA

OHIO	4856 SQ. MI.
INDIANA	1260 SQ. MI.
MICHIGAN	470 SQ. MI.
TOTAL IN BASIN	6586 SQ. MI.

MAUMEE RIVER DRAINAGE BASIN

LOCATION PLAN
MAUMEE RIVER DRAINAGE BASIN

10 0 10 20
SCALE IN MILES

Correlations with the Literature

Research of the literature was not, in general, helpful, because the small amount of information available about plants concerns primarily trees and common vegetables, because of analyses for elements other than those considered here, and because nowhere is the basis for "normal" concentrations defined.

In several cases there were reports of analyses of plants similar to the plant types considered in this project, and for some of the same elements for which data have been given here. In these cases, correlations were attempted, but with few satisfactory results. In the few cases that the data from the literature were in near agreement with the values presented here, there were found direct contradictions in the literature. This makes valid correlations questionable. Some exampels will clarify this.

Listed below are values given as "normal" concentrations for certain elements in scrub birch trees and some common vegetables as reported in several different articles.

H.V. Warren in his article, "Biogeochemistry in Canada", cites normal values for copper and lead in scrub birch trees as:

Cu --- 480 ppm

Pb --- 25-100 ppm

In another article, "Variations in the Trace Element Contents of Some Vegetables", Warren calls the following concentrations

"normal":

Lettuce:	Cu ---	60 ppm
	Pb ---	20 ppm
Cabbage:	Cu ---	40 ppm
	Pb ---	16 ppm
Potato :	Cu ---	100 ppm
	Pb ---	40 ppm
Carrot :	Cu ---	70 ppm
	Pb ---	30 ppm

In yet another article, "A Study in Lead Pollution", Warren, along with R. Delavualt, K. Fletcher, and E. Wilks, presents the following values taken from the Canadian Food and Drug Directorate as "normal" for lead:

Potato:	Pb ---	less than .6 ppm
"Leafy Vegetable":	Pb ---	.5 ppm
"Root Vegetable" :	Pb ---	.4 ppm

John Harley in Environmental Sciences and Technology gives the following values for "normal" concentrations of lead:

Potato:	Pb ---	.17 ppm
"Root Vegetable":	Pb ---	.07 ppm

The contradictions in the above data should be apparent.

In attempts at correlation, I have used the milligrams per liter (mg/l) values given in the appendix so as to agree with the parts per million (ppm) values given in the literature, and I have attempted to use samples close to the same type of plants cited in the literature. For example, starchy cattail roots might very well concentrate trace elements in the same manner as potatoes or "root vegetables", tree

branches the same as scrub birch trees, and dandelions the same as lettuce, cabbage, or "leafy vegetables".

The following values were compared with those for potatoes or "root vegetables":

O-1 (ROOTS)	Cu --- 2.392 mg/l Pb --- 0.482 mg/l
M-28 (CATTAIL ROOTS)	Cu --- 4.703 mg/l Pb --- 0.157 mg/l
O-35 (ROOTS)	Cu --- 30.687 mg/l Pb --- Trace
Bac-45 (CATTAIL ROOTS-- used as normal in this work)	Cu --- 0.974 mg/l Pb --- 0.284 mg/l

For comparison with scrub birch trees' values:

O-2 (TREE BRANCHES)	Cu --- 4.078 mg/l Pb --- 1.841 mg/l
O-4 (TREE BRANCHES)	Cu --- 4.382 mg/l Pb --- 1.743 mg/l
O-6 (TREE BRANCHES)	Cu --- 3.570 mg/l Pb --- 1.955 mg/l
O-7 (TREE BRANCHES)	Cu --- 1.178 mg/l Pb --- ---
M-30 (TREE BRANCHES)	Cu --- Trace Pb --- Trace
M-32 (TREE BRANCHES)	Cu --- 14.353 mg/l Pb --- 6.312 mg/l
O-41 (TREE BRANCHES)	Cu --- Trace Pb --- 0.000 mg/l

For comparison with cabbage, lettuce, and "leafy vegetables":

B-13 (DANDELIONS)	Cu --- 0.221 mg/l Pb --- 0.277 mg/l
B-15 (DANDELIONS)	Cu --- 0.171 mg/l Pb --- 0.277 mg/l
Bac-46 (DANDELIONS-- used as normal in this work)	Cu --- 2.030 mg/l Pb --- 0.681 mg/l

To repeat, these comparisons showed good agreement in some cases, but very great variation in others. As a result, the above values are mentioned here for general information only, and no conclusions will be drawn from them.

SUMMARY AND CONCLUSION

A descriprion of sample collection and the reasoning involved have been given. A critique of several methods of sample preparation was made, and the nitric acid-hydrogen peroxide method found to be the most efficient. The data collected has been organized and presented with maximum and minimum values noted and the mean value for each element calculated. Some correlations were attempted, both within the data collected from this research, and with data obtained from the literature.

In order to draw conclusions from a body of data such as has been collected here, there must be a certain amount of consistency or a number of absolutes upon which conclusions may be based. Although some general trends were detected in the data, it has been found that the number of variables involved prohibits the formulation of any conclusions except one.

Besides the small number of samples taken to represent

an area of approximately 5,000 square miles, there are several other factors which tend against consistency within the data. It has been found that plants concentrate trace elements in an extremely differential manner. That is, for example, one plant may concentrate copper but not cadmium. Another may concentrate cadmium but not copper, while a third concentrates both, and a fourth neither. In actuality, none of these necessarily reflects the concentration of trace elements in the plants' environment. The fact that different plants concentrate elements in different amount is not considered a conclusion in itself because not enough information is present here to detect any proportional (or other) relationship upon which to base suspicion of a pattern.

Just as varying rates of flow may cause dilution or concentration of trace elements in river water, and just as periodic dumping of industrial and municipal wastes may cause concentration fluctuations, so also may the concentrations of trace elements in plants vary. As often as the temperature and pH of the river water changes, the concentrations of the elements in question may vary. As numerous as the possibilities for variation are the possible sources of trace elements for introduction into the hydrologic system. In their Senior Theses work concerning the trace element concentrations in water and sediment from the Maumee Basin, Richard Bowen and Roger Webb have cited numerous possibilities for sources of industrial, automotive, and agricultural trace element

pollution. David Birsa has done a Senior Thesis confirming the possibility of the carbonate bedrock of the Maumee Basin as a trace element source.

Therefore, it should be evident that these and many other variables introduced by the geochemistry, biochemistry, and plant physiology involved make it exceedingly difficult to draw valid conclusions. There is one, however, and apparently only one so far, that is definite. This project has shown that plants do concentrate trace elements, and in many cases the concentration is in some way dependent upon the concentration present in the plants' water source. As a result, plants do affect the concentration of trace elements in a hydrologic system by removing these elements, sometimes in substantial amounts.

BIBLIOGRAPHY

Burrell, D. C. (1968), "Atomic Absorption Spectrophotometry in the Field of Marine Research," A. A. Newsletter, vol. 7, no. 4, July-August.

Harley, J. H. (1970), Environmental Sciences and Technology, vol. 4, no. 3:225.

Warren, H. V. (1972), "Biogeochemistry in Canada," Endeavour, vol. XXXI, no. 112, January, pp. 46-49.

_____, et al. (1972), "Variations in the Trace Element Content of Some Vegetables," J. Roy. Coll. Gen. Practit., vol. 22, no. 56.

_____, et al. (1971), "A Study in Lead Pollution," Western Miner, February.